Catalysis by *L*-Lysine: A Green Method for the Condensation of Aromatic Aldehydes with Acidic Methylene Compounds in Water at Room Temperature

Zhang, Yan(张岩) Sun, Cuizhi(孙翠枝) Liang, Jun(梁军) Shang, Zhicai*(商志才)

Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang 310027, China

The condensation of aromatic aldehydes with acidic methylene compounds such as ethyl benzoylacetate, 2,4-pentanedione and dimedone proceeded efficiently in pure water in the presence of *L*-lysine at room temperature. Interestingly, there are two different reaction mechanisms taking place under the same green catalyst system. This provides a green and mild synthetic method for the preparation of these two classes of compounds.

Keywords condensation, aldehyde, *L*-lysine, xanthenedione, green chemistry

Introduction

In recent years, there has been an increased demand for “clean” and environmentally friendly reactions in chemistry, which is essential to the sustainable development of our society. Especially in organic chemistry, synthesis is mainly carried out in the presence of catalyst in the solution phase. Nowadays catalysis has to face new challenges, including the ability to meet sustainability criteria, and once it is translated into chemical words, it means the implementation of the twelve green chemistry principles.[1] Organo-catalysis became a new research area in synthetic chemistry several years ago, which is one of the most important contents for green chemistry. Driven by environmental concerns, there are great interest and need for cheap and readily available, recyclable and reusable nonmetallic small-molecule catalysts that promote reactions to expand the scope of organocatalysis, which obviously is an environmentally benign approach to fine chemical synthesis, especially large scale reactions. Organic solvents are still the main choice in modern organic synthesis. But these solvents are often problematic because of their toxicity, flammability, or environmental hazards. Fortunately, in recent years, there has been increased recognition that organic reactions carried out in aqueous media may offer advantages over those occurring in organic solvents.[2] So switching from organic solvents to water as reaction medium is a challenging and attractive task for synthetic chemists. We concentrate our attention on using water instead of organic solvent in chemical processes.

In our recent studies, we have found that the basic amino acids *L*-lysine in pure water is an efficient and reusable green catalyst system for condensations of aromatic aldehydes with many acidic methylene compounds. Knoevenagel condensation is one of the important reactions of organic chemistry and its synthetic utility has special place of significance in organic synthesis, for it is largely employed to form C—C bonds for the synthesis of unsaturated compounds. For example, *α*,*β*-enones are synthetically important organic molecules, which are generally used as substrates for Diels-Alder reactions, Michael addition and Morita-Baylis-Hillman reactions.[3] Knoevenagel condensations are usually carried out in the presence of base,[4] Lewis acid,[5] surfactants,[6] zeolites,[7] grinding,[8] metal ions[9] and alkali metal modified NbMCM-41 have also been employed to catalyze this reaction.[10] However, these methods suffer from many limitations such as harsh reaction conditions, the use of harmful organic solvents, requirement of high temperatures, and in some reactions the catalysts can not be reused. Similarly, the use of ionic liquids[11] paves a new path for the condensation. Yet, the application of ionic liquids in the industrial syntheses of fine chemicals is still problematic because of the relatively high cost of these solvents. Xanthenediones, a group of synthetically and biologically important compounds, constitute a structural unit in a number of natural products and have been used as versatile synthons due to the inherent reactivity of the inbuilt pyran ring. Obviously, xanthenediones can be simply obtained by dehydration cyclization from their ring-opening derivatives **4**. Recently, several reports have been put forward in which xanthenedione derivatives were obtained through condensation of aldehyde and 5,5-dimethyl-1,3-cyclohexanedione (dimedone) under various conditions.[12] Similarly, taking their limitations into account, to develope novel and practical methods for the preparation of xanthenedione and its derivatives is still necessary. To the best of our knowledge, there is no report of the application of lysine

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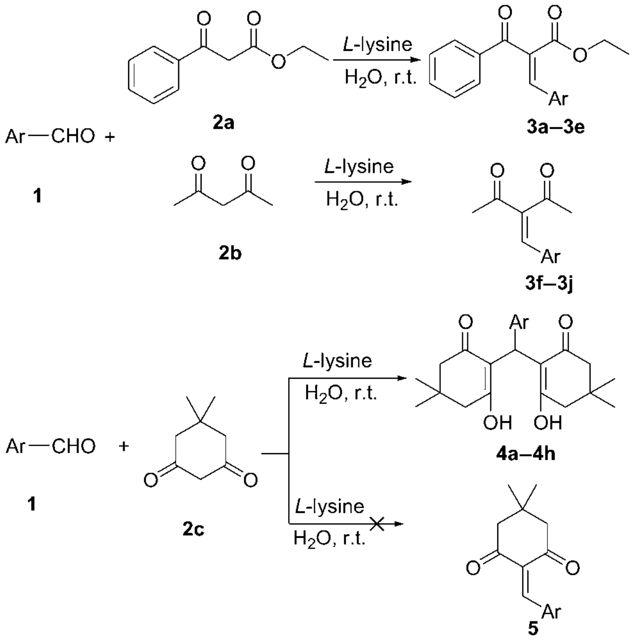
* E-mail: shangzc@zju.edu.cn; Fax: 0086-0571-87951895

Received March 20, 2010; revised May 14, 2010; accepted August 11, 2010.

for these condensations. In this paper, we will report that *L*-lysine dissolved in water is an efficient catalyst system for these two types of condensation reaction as shown in Scheme 1.

Scheme 1 The condensation of aromatic aldehydes with acidic methylene compounds



Results and discussion

As we know, *L*-lysine, a cheap basic amino acid, can easily dissolve in water. But it can hardly dissolve in organic solvents, such as ether, ethyl acetate and even acetone. Therefore, it is easy to get the product from the reaction system by extraction. We first applied this green catalyst system in the reaction of aromatic aldehydes **1** with acidic methylene compounds **2a**—**2b** as shown in Table 1. The results show that ethyl benzoylacetate is more likely to carry out Knoevenagel reaction in water than 2,4-pentanedione in the presence of *L*-lysine. The electron-deficient aldehydes proceeded much better and faster than the electron-rich ones.

Table 1 The results for the Knoevenagel condensation between aromatic aldehydes **1** and dicarbonyl compounds **2a**—**2b** in water

Entry	Ar	Dicarbonyl compound	Time/h	Product	Yield[a]/%
1	2-$NO_2C_6H_4$	**2a**	28	**3a**	82 (11)[b]
2	3-$NO_2C_6H_4$	**2a**	30	**3b**	82
3	4-$NO_2C_6H_4$	**2a**	30	**3c**	80
4	4-CNC_6H_4	**2a**	30	**3d**	79
5	4-$CH_3OC_6H_4$	**2a**	34	**3e**	68
6	3-BrC_6H_4	**2b**	50	**3f**	61
7	4-$NO_2C_6H_4$	**2b**	48	**3g**	64
8	4-ClC_6H_4	**2b**	50	**3h**	60
9	4-$CH_3C_6H_4$	**2b**	54	**3i**	58
10	4-$CH_3OC_6H_4$	**2b**	54	**3j**	62

[a] Isolated yields after column chromatography; [b] reactions performed with no addition of *L*-lysine.

On the basis of these observations, we then extended the reactions of aldehydes to other dicarbonyl compound. Dimedone (**2c**) was investigated. Surprisingly, contrary to our expectation, the initial Knoevenagel products **5** are not formed, only **4** is obtained in excellent yield (Table 2), which is in contrast to other reported examples.[13,14] That's to say, there are two very different reaction mechanisms taking place in the same reaction conditions.

Table 2 The results on the reaction of aromatic aldehydes **1** with dimedone (**2c**) in water at room temperature catalyzed by *L*-lysine

Entry	Ar	Time/h	Product	Yield[a]/%
11	4-$NO_2C_6H_4$	5	**4a**	95
12	4-CNC_6H_4	5	**4b**	92
13	4-BrC_6H_4	6	**4c**	91
14	3-BrC_6H_4	6	**4d**	92
15	4-ClC_6H_4	6	**4e**	90
16	C_6H_5	7	**4f**	89
17	4-$CH_3C_6H_4$	9	**4g**	90
18	4-$CH_3OC_6H_4$	9	**4h**	88

[a] Isolated yields after column chromatography.

This result prompted us to reflect on the different mechanisms of the two type condensations (Scheme 2 and Scheme 3), especially the latter. Some people think that the initial Knoevenagel product is an intermediate, then the Michael addition carries out to form **4**.[6,12c] We also think so, but it is hard to explain why **3** does not occur Michael addition even if **2a**—**2b** are excessive.

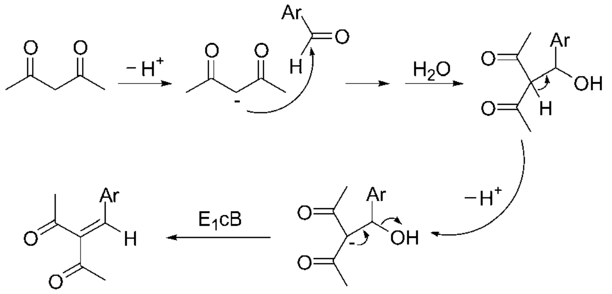
Conclusions

In conclusion, we have developed a clean, inexpensive, efficient and reusable methodology to carry out two types of condensations between aromatic aldehydes and dicarbonyl compounds in water. The catalyst of *L*-lysine was found to be a mild and effective catalyst. Efforts are underway to elucidate the mechanistic details of the condensation and disclose its scope and limitations.

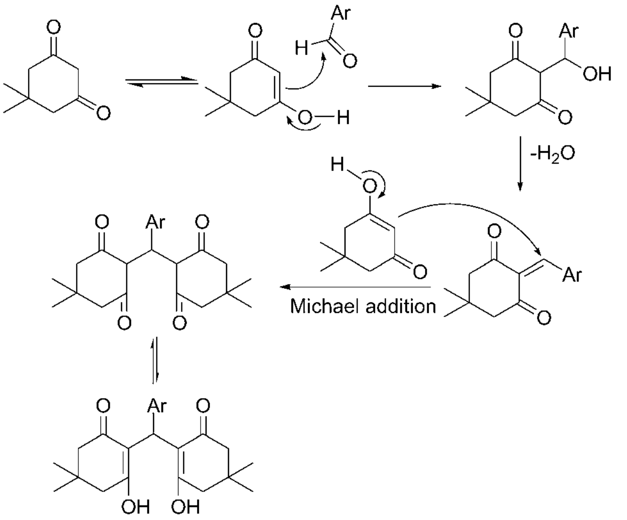
Experimental

In a typical experimental procedure, a mixture of an aldehyde **1** (1 mmol), acidic methylene compound **2a**—**2b** (1 mmol) or **2c** (2 mmol), and *L*-lysine (20 mol%) in 4 mL of water was stirred in a 10 mL, round-bottomed flask at ambient temperature. The reaction was followed and monitored by TLC. When the reaction was completed, ethyl acetate or dichloromethane (5 mL×3) was added into the flask to extract the product. Then the reaction mixture was partitioned between aqueous and

Scheme 2 Mechanism of the Knoevenagel condensation reaction

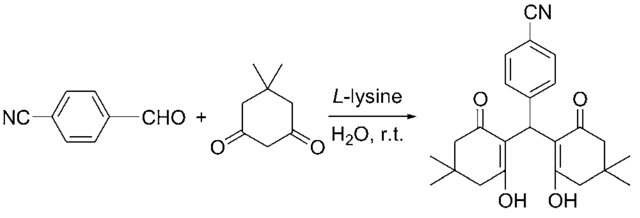


Scheme 3 Proposed reaction steps that take place in the condensation between the aromatic aldehydes and dimedone



organic phase. The organic layer was separated and concentrated, then the residue was purified by column chromatography eluting with petroleum/ethyl acetate or ethyl acetate/dichloromethane to give the condensation product. We also investigated the reusability of this catalyst system. After the reaction was completed, the product was extracted out by filling in ethyl acetate or dichloromethane. Amazingly, the aqueous solution could be reused without any loss of its activity even after five runs (Table 3).

Table 3 Recycling experiments with *L*-lysine[a]



Run	1	2	3	4	5
Yield[b]/%	92	90	91	89	89

[a] Reactions performed with *p*-cyanobenzaldehyde (1 mmol), dimedone (2 mmol), and *L*-lysine (20 mol%) in pure water (4 mL) and stirred for 5 h at r.t. [b] Isolated yields after column chromatography.

The physical and spectra data of the compounds are as follows.

The process of reactions was monitored by TLC on silica. ^{1}H NMR and ^{13}C NMR spectra were recorded with TMS as internal standard using a Bruker AMX-500 MHz spectrometer at 500 and 125 MHz, respectively. IR spectra were measured with a Nicolet Nexus FTIR 670 spectrophotometer. Low-resolution MS analyses were measured on a Bruke Esquire 3000 spectrometer using ESI (electrospray ionization) technique.

Ethyl 2-benzoyl-3-(2-nitrophenyl)acrylate (3a) White solid; m.p. 106—108 ℃; R_f=0.43 *V*(EtOAc)∶*V*(petroleum)=1∶5; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.32 (s, 1H), 8.04 (d, *J*=7.93 Hz, 1H), 7.83 (t, *J*=7.34 Hz, 2H), 7.45—7.47 (m, 2H), 7.40 (t, *J*=7.51 Hz, 2H), 7.33 (t, *J*=7.72 Hz, 2H), 4.28 (q, *J*=7.11 Hz, 2H), 1.24 (t, *J*=7.11 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 193.9, 164.3, 147.4, 140.0, 136.5, 134.3, 134.1, 134.0, 131.6, 130.3, 130.1, 129.2, 128.9, 125.1, 62.0, 14.2; IR (KBr) v: 2985, 1716, 1668, 1601, 1560, 1525, 1344, 1253, 1233, 1201, 801, 727 cm^{-1}; MS (ESI) *m/z*: 325.9 ([M+H])$^+$.

Ethyl 2-benzoyl-3-(3-nitrophenyl)acrylate (3b) White solid; m.p. 94—96 ℃; R_f=0.40 *V*(EtOAc)∶*V*(petroleum)=1∶5; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.22 (s, 1H), 8.11 (q, *J*=6.7 Hz, 1H), 7.98 (s, 1H), 7.94 (d, *J*=7.3 Hz, 2H), 7.66 (d, *J*=7.8 Hz, 1H), 7.57 (d, *J*=7.4 Hz, 1H), 7.41—7.47 (m, 3H), 4.26 (q, *J*=7.2 Hz, 2H), 1.20 (t, *J*=7.1 Hz, 3H); IR (KBr) v: 3084, 1712, 1663, 1619, 1595, 1528, 1450, 1353, 1251, 1205, 1096, 809, 737 cm^{-1}; MS (ESI) *m/z*: 325.9 ([M+H])$^+$.

Ethyl 2-benzoyl-3-(4-nitrophenyl)acrylate (3c) White solid; m.p. 100—102 ℃; R_f=0.36 *V*(EtOAc)∶*V*(petroleum)=1∶6; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.09 (d, *J*=8.8 Hz, 2H), 7.98 (s, 1H), 7.92 (q, *J*=8.0 Hz, 2H), 7.58 (d, *J*=7.4 Hz, 1H), 7.52 (t, *J*=1.7 Hz, 2H), 7.45 (t, *J*=7.8 Hz, 2H), 4.26 (q, *J*=7.1 Hz, 2H), 1.19 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 194.0, 164.4, 148.4, 139.6, 139.3, 135.9, 135.7, 134.6, 130.8, 129.3, 128.9, 124.1, 62.3, 14.2; IR (KBr) v: 1723, 1673, 1596, 1519, 1449, 1346, 1250, 1231, 1197, 851, 692 cm^{-1}; MS (ESI) *m/z*: 348.2 ([M+Na])$^+$.

Ethyl 2-benzoyl-3-(4-cyanophenyl)acrylate (3d) Pale-yellow oil; R_f=0.26 *V*(EtOAc)∶*V*(petroleum)=1∶4; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.91 (q, *J*=6.3 Hz, 3H), 7.59 (t, *J*=7.5 Hz, 1H), 7.52 (d, *J*=8.4 Hz, 2H), 7.44—7.47 (m, 4H), 4.24 (q, *J*=7.1 Hz, 2H), 1.18 (t, *J*=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 194.7, 164.5, 140.1, 137.4, 135.9, 135.0, 134.5, 133.1, 132.6, 130.4, 130.1, 129.2, 118.2, 62.2, 14.1; IR (KBr) v: 2985, 2230, 1721, 1673, 1627, 1596, 1581, 1501, 1449, 1368, 1252, 1016, 832, 689 cm^{-1}; MS (ESI) *m/z*: 305.9 ([M+H])$^+$.

Ethyl 2-benzoyl-3-(4-methoxyphenyl)acrylate (3e) Yellow oil; R_f=0.51 *V*(EtOAc)∶*V*(petroleum)=1∶4; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.96 (t, *J*=7.3 Hz, 2H), 7.90 (s, 1H), 7.55 (s, 1H), 7.43 (t, *J*=7.9 Hz, 2H), 7.31 (d, *J*=8.8 Hz, 2H), 6.75 (d, *J*=8.8 Hz, 2H), 4.20 (q, *J*=

7.1 Hz, 2H), 3.74 (s, 3H), 1.16 (t, J＝7.1 Hz, 3H); IR (KBr) ν: 2979, 1716, 1673, 1601, 1513, 1449, 1306, 1251, 1175, 1027, 831, 690 cm^{-1}.

3-(3-Bromobenzylidene)pentane-2,4-dione (3f) Yellow oil; R_f＝0.52 V(EtOAc) ∶ V(petroleum)＝1 ∶ 4; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 7.54 (q, J＝1.8 Hz, 2H), 7.40 (s, 1H), 7.32 (s, 1H), 7.27 (d, J＝8.1 Hz, 1H), 2.42 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ: 205.0, 196.4, 144.1, 138.0, 135.2, 133.6, 132.7, 130.7, 128.0, 123.3, 31.8, 26.8; IR (KBr) ν: 2997, 2919, 1711, 1662, 1618, 1561, 1473, 1419, 1381, 1278, 1241, 1179, 1075, 785, 686 cm^{-1}; MS (ESI) m/z: 291.0 ([M＋Na])$^+$.

3-(4-Nitrobenzylidene)pentane-2,4-dione (3g) Yellow oil; R_f＝0.47 V(EtOAc) ∶ V (petroleum)＝1 ∶ 4; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 8.25 (d, J＝8.7 Hz, 2H), 7.57 (d, J＝8.7 Hz, 2H), 7.51 (s, 1H), 2.47 (s, 3H), 2.30 (s, 3H); IR (KBr) ν: 3105, 3069, 1712, 1661, 1597, 1520, 1418, 1347, 1237, 1175, 862, 752, 691 ㎝$^{-1}$.

3-(4-Chlorobenzylidene)pentane-2,4-dione (3h) White solid; m.p. 75—76 ℃; R_f＝0.51 V(EtOAc) ∶ V(petroleum)＝1 ∶ 5; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 7.41 (s, 1H), 7.36 (d, J＝8.7 Hz, 2H), 7.33 (d, J＝8.7 Hz, 2H), 2.41 (s, 3H), 2.28 (s, 3H); IR (KBr) ν: 2997, 1710, 1659, 1616, 1590, 1490, 1421, 1384, 1356, 1309, 1282, 1242, 1175, 1093, 1012, 823 cm^{-1}.

3-(4-Methylbenzylidene)pentane-2,4-dione (3i) Pale-yellow oil; R_f＝0.51 V(EtOAc) ∶ V(petroleum)＝1 ∶ 4; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 7.46 (s, 1H), 7.29 (d, J＝8.2 Hz, 2H), 7.20 (d, J＝8.0 Hz, 2H), 2.41 (s, 3H), 2.38 (s, 3H), 2.30 (s, 3H); IR (KBr) ν: 2919, 1709, 1658, 1605, 1507, 1419, 1386, 1350, 1246, 1173, 813 cm^{-1}.

3-(4-Methoxybenzylidene)pentane-2,4-dione (3j) Pale-yellow oil; R_f＝0.38 V(EtOAc) ∶ V(petroleum)＝1 ∶ 4; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 7.43 (s, 1H), 7.36 (d, J＝8.8 Hz, 2H), 6.91 (d, J＝7.0 Hz, 2H), 3.85 (s, 3H), 2.41 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ: 206.4, 196.7, 162.0, 141.0, 140.0, 132.1, 125.6, 114.8, 55.7, 31.9, 26.6; IR (KBr) ν: 2925, 2835, 1709, 1654, 1600, 1570, 1513, 1423, 1307, 1260, 1172, 1028, 830 cm^{-1}.

2,2'-[(4-Nitrophenyl)methylene]bis(3-hydroxy-5,5-dimethylcyclohex-2-enone) (4a) Yellow solid; m.p. 169—171 ℃; R_f＝0.23 V(EtOAc) ∶ V(petroleum)＝1 ∶ 4; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 11.94 (broad signal, OH), 8.12 (d, J＝8.4 Hz, 2H), 7.25 (d, J＝7.8 Hz, 2H), 5.56 (s, 1H), 2.31—2.46 (m, 8H), 1.11 (s, 6H), 1.06 (s, 6H); IR (KBr) ν: 3435, 2958, 1594, 1513, 1468, 1451, 1375, 1345, 1252, 1167, 1154, 1044, 852 cm^{-1}.

4-[Bis(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)methyl]benzonitrile (4b) Pale-yellow solid; m.p. 164—166 ℃; R_f＝0.56 V(EtOAc) ∶ V(petroleum)＝1 ∶ 4; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 11.86 (broad signal, OH), 7.56 (d, J＝8.3 Hz, 2H), 7.19 (d, J＝8.1 Hz, 2H), 5.52 (s, 1H), 2.31—2.46 (m, 8H), 1.22 (s, 6H), 1.11 (s, 6H); IR (KBr) ν: 3484, 2964, 2887, 2225, 1594, 1501, 1447, 1375, 1306, 1253, 1120, 842 cm^{-1}.

2,2'-[(4-Bromophenyl)methylene]bis(3-hydroxy-5,5-dimethylcyclohex-2-enone) (4c) Yellow solid; m.p. 172—174 ℃; R_f＝0.45 V(EtOAc) ∶ V(petroleum)＝1 ∶ 5; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 11.86 (s, 1H, OH), 7.37 (d, J＝8.6 Hz, 2H), 6.95 (d, J＝8.0 Hz, 2H), 5.45 (s, 1H), 2.33—2.44 (m, 8H), 1.21 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ: 190.9, 189.6, 137.5, 131.5, 128.8, 119.9, 115.5, 47.3, 46.7, 32.7, 31.7, 29.8, 27.7; IR (KBr) ν: 3420, 2958, 1594, 1486, 1468, 1450, 1373, 1304, 1265, 1167, 898, 825 cm^{-1}; MS (ESI) m/z: 448.8 ([M＋H])$^+$.

2,2'-[(3-Bromophenyl)methylene]bis(3-hydroxy-5,5-dimethylcyclohex-2-enone) (4d) Pink solid; m.p. 184—186 ℃; R_f＝0.50 V(EtOAc) ∶ V(petroleum)＝1 ∶ 4; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 11.88 (broad signal, OH), 7.29 (t, J＝7.8 Hz, 1H), 7.23 (s, 1H), 7.13 (t, J＝7.8 Hz, 1H), 7.01 (d, J＝7.8 Hz, 1H), 5.49 (s, 1H), 2.29—2.48 (m, 8H), 1.22 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ: 190.9, 189.7, 141.0, 130.4, 129.9, 129.2, 125.7, 122.7, 115.3, 47.3, 46.7, 32.9, 31.7, 29.8, 27.6; IR (KBr) ν: 3447, 2955, 2869, 1597, 1471, 1419, 1377, 788, 725 cm^{-1}; MS (ESI) m/z: 447.2 ([M＋H])$^+$, 446.8 ([M－H])$^-$.

2,2'-[(4-Chlorophenyl)methylene]bis(3-hydroxy-5,5-dimethylcyclohex-2-enone) (4e) White solid; m.p. 139—141 ℃; R_f＝0.46 V(EtOAc) ∶ V(petroleum)＝1 ∶ 4; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 11.86 (s, 1H, OH), 7.22 (d, J＝8.6 Hz, 2H), 7.01 (d, J＝8.4 Hz, 2H), 5.47 (s, 1H), 2.29—2.48 (m, 8H), 1.21 (s, 6H), 1.10 (s, 6H); IR (KBr) ν: 3435, 2958, 2872, 1595, 1490, 1468, 1374, 1304, 1253, 830 cm^{-1}.

2,2'-(Phenylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-enone) (4f) White solid; m.p. 190—192 ℃; R_f＝0.50 V(EtOAc) ∶ V(petroleum)＝1 ∶ 4; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 11.89 (s, 1H, OH), 7.26 (q, J＝7.6 Hz, 2H), 7.17 (d, J＝7.0 Hz, 1H), 7.09 (d, J＝8.1 Hz, 2H), 5.54 (s, 1H), 2.29—2.48 (m, 8H), 1.23 (s, 6H), 1.10 (s, 6H); IR (KBr) ν: 3450, 2962, 2872, 1594, 1492, 1448, 1375, 1302, 1251, 1164, 845, 777, 695 cm^{-1}.

2,2'-(*p*-Tolylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-enone) (4g) Yellow solid; m.p. 126—128 ℃; R_f＝0.52 V(EtOAc) ∶ V(petroleum)＝1 ∶ 4; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 11.90 (broad signal, OH), 7.07 (d, J＝8.0 Hz, 2H), 6.97 (d, J＝7.8 Hz, 2H), 5.50 (s, 1H), 2.29—2.47 (m, 11H), 1.22 (s, 6H), 1.09 (s, 6H); IR (KBr) ν: 2958, 2871, 1714, 1596, 1511, 1450, 1372, 1305, 1041, 813 cm^{-1}.

2,2'-[(4-Methoxyphenyl)methylene]bis(3-hydroxy-5,5-dimethylcyclohex-2-enone) (4h) White solid; m.p. 142—144 ℃; R_f＝0.43 V(EtOAc) ∶ V(petroleum)＝1 ∶ 4; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 11.91 (s, 1H, OH), 6.99 (d, J＝8.4 Hz, 2H), 6.81 (d, J＝8.7 Hz, 2H), 5.48 (s, 1H), 3.77 (s, 3H), 2.29—2.47 (m, 8H), 1.22 (s, 3H), 1.09 (s, 3H); IR (KBr) ν: 3452, 2959, 1593, 1509, 1467, 1452, 1417, 1375, 1305, 1248, 1179, 1034, 830 cm^{-1}.

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(E1003201 Cheng, B.; Zheng, G.)